PB82-251265

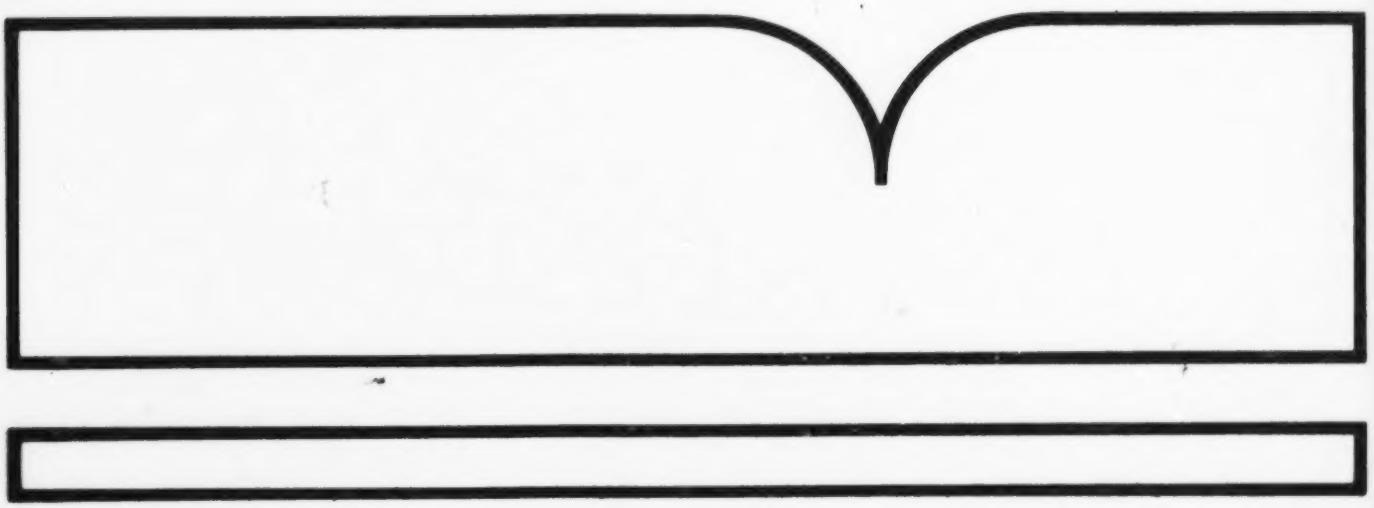
Growth and Dissipation of Pesticide Oxons

Agricultural Research and Education Center
Lake Alfred, FL

Prepared for

Health Effects Research Lab.
Research Triangle Park, NC

18 Jul 81



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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA 600/J-82-210	2. JOURNAL ARTICLE	3. RECIP PB82-251265

4. TITLE AND SUBTITLE
Growth and Dissipation of Pesticide Oxons

5. REPORT DATE

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Agricultural Research and Education Center
University of Florida
700 Experiment Station Road
Lake Alfred, FL 33850

10. PROGRAM ELEMENT NO.
CCAE1A

11. CONTRACT/GRANT NO.
Grant No. R806474

12. SPONSORING AGENCY NAME AND ADDRESS
Office of Research and Development (RTP,NC)
Health Effects Research Laboratory
US Environmental Protection Agency
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA-600/11

15. SUPPLEMENTARY NOTES
Published In: Bulletin of Environmental Contamination & Toxicology 27: 512-517, 1981

16. ABSTRACT

Progress toward a solution to the worker reentry problem requires a method for predicting the conversion of applied organophosphate pesticides to their oxon analogs, together with subsequent oxon persistence. That oxons are more toxic than their parent compound is well known. For example, paraoxon is ten times more toxic intravenously and fifty-five times more toxic dermally than the same amount of parathion (NABB et.al. 1966). In some regions of the United States, it is not unusual for the oxon level to exceed that of the parent at some point in the growth-decay process of the oxon on the plant or soil surface.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

Bull. Environm. Contam. Toxicol. 27, 512-517 (1981)

EPA 600/J-82-210

Growth and Dissipation of Pesticide Oxons[1,2]

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Progress toward a solution to the worker reentry problem requires a method for predicting the conversion of applied organophosphate pesticides to their oxon analogs, together with subsequent oxon persistence. That oxons are more toxic than their parent compound is well known. For example, paraoxon is ten times more toxic intravenously and fifty-five times more toxic dermally than the same amount of parathion (NABB et al. 1966). In some regions of the United States, it is not unusual for the oxon level to exceed that of the parent at some point in the growth-decay process of the oxon on the plant or soil surface.

The kinetics of these two distinct processes should be accurately described as to mathematical form before oxon growth and decay can be predicted, even though the physico-chemical details may not yet be understood. Were this description not too complicated, only a few numbers could characterize any oxon level-vs-time curve. Then whatever influence such factors as pesticide type, application rate, crop, soil, climate or agricultural practices had on these numbers could be systematically determined. Some predictability would result so that enlightened management procedures might be established to protect fieldworkers.

Oxon growth and dissipation has been modeled by several researchers. POPENDORF and LEFFINGWELL (1978) used five variable coefficients to characterize paraoxon levels, whereas SPEAR et al. (1975) used three. Both employed a first-order approach with fits made to paraoxon and parathion data from California citrus foliage. Importantly, both models assumed paraoxon growth to be strictly proportional to parathion decay.

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[1]Florida Agricultural Experiment Stations Journal Series No. 3153.
[2]Supported by Environmental Protection Agency Research Grant R806474.

0007-4861/81/0027-0512 $01.20
1981 Springer-Verlag New York Inc.

Their predicted levels departed by about 15% from those observed.

Purpose

We suggest a model, also first-order, but without the constraint that the oxon growth rate and the parent decay rate be proportional. While the two are no doubt related, evidence for a proportional relationship is not strong. In fact, there is considerable contrary evidence (see below).

Our general approach has been to investigate parent and oxon curves separately. Then, whether linkage exists between the two becomes apparent from a comparison of the two independent investigations.

Previously, STAMPER et al. (1979) presented a model of parent dissipation showing that an inverse power description is superior to an exponential (first-order) one. But since parent dissipation usually involves more dominant pathways than conversion into oxons, oxon growth still may be presumed to be exponential, although not related a priori to the parent.

Model

The model itself is uncomplicated. With N representing oxon concentration, the differential equation is

$$\dot{N} = Ac \exp(-ct) - bN \qquad (1)$$

with A, c and b constants chosen to optimize the fit to data. Equation 1 means only that oxon decay is first-order and its growth rate exponential. It has the solution

$$N = [Ac/(c-b)]\,[\exp(-bt) - \exp(-ct)] \qquad (2)$$

As to the interpretation of the constants: c is the rate constant for growth, b the rate constant for decay, and A represents the total amount of oxon created irrespective of oxon loss. This last can be seen from Equation 1 by integrating its growth part from 0 to ∞.

Agreement with Experiment

Models are best constructed from or tested with data which are regular; i.e., data points through which smooth curves can be drawn, suggestive of little measurement error. Regular oxon data can usually be very

well represented by Equation 2. Four such examples, typical of the several constructed, appear in Fig. 1. They have been selected in part to show the versatility of the model regarding oxon type, surface to which the parent was applied, and initial parent concentration.

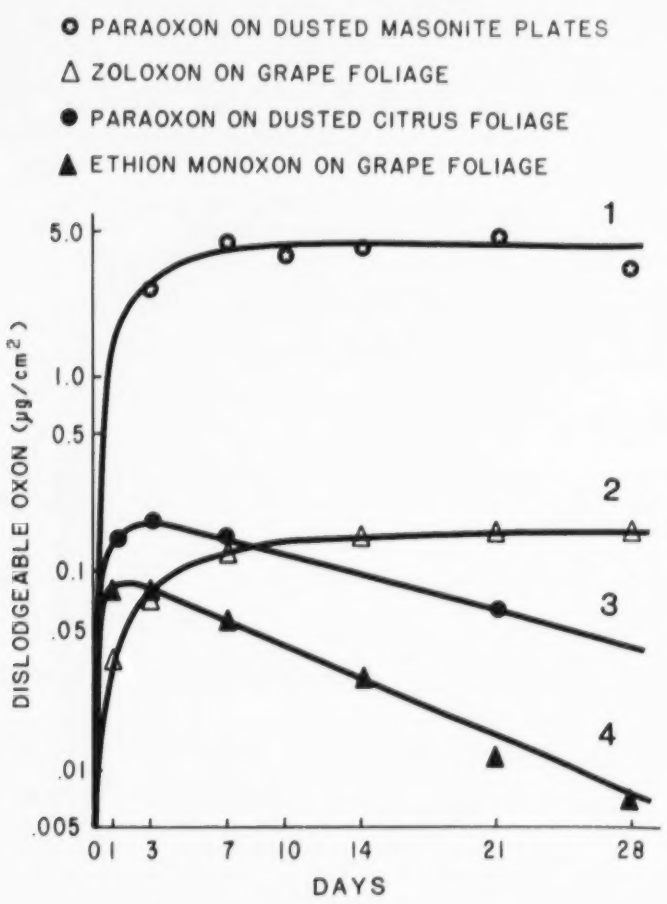

Fig. 1. Oxon growth-decay curves fitted to experimental data according to $N = [Ac/(c-b)] [\exp(-bt) - \exp(-ct)]$. N = oxon level, c = oxon growth rate constant, b = oxon decay rate constant, A = total oxon created irrespective of loss, and t = time.

Data groups 1 and 3 are taken from WINTERLIN et al. (1981) and groups 2 and 4 from LEFFINGWELL et al. (1975). The fit (solid line) in each case is nearly exact. Maximum oxon levels are reached at days 1, 3, 16, and > 28 depending on data group. These four oxon data groups are rather typical of oxon behavior. Similar data to 1 and 2 in general features were obtained by ADAMS (1976) from conversion of parathion to paraoxon on dusted citrus leaves. More like sets 3 and 4 were those obtained by POPENDORF et al. (1978) and SPEAR et al. (1975), respectively.

Curve Constants

The constants (Table 1) were determined by trial and error, a process which goes quickly after a little practice. They vary considerably with data group. Oxon level prediction, of course, awaits an understanding of what determines each constant's value.

As for constant "A", it is unsurprisingly linked to N_o, the parent concentration at day 0. The ratio A/N_o gives the fraction of parent ultimately converted into oxon. It averages about 12% for the curves of Fig. 1, but this percentage cannot be regarded as anything but order-of-magnitude since it is based upon only four curves. The correlation, however, between "A" and "N_o" is 0.99 which is significant.

The constant "b" correlates poorly (R = 0.64) with "k", suggesting that factors governing dislodgeable oxon dissipation are different than for the parent. But there is also the possibility that parent dissipation is so poorly described by an exponential rate constant (k) that no good correlation could be expected, whatever the case.

If oxon growth were proportional to parent decay, c would equal k. This is not at all the case (Table 1). Furthermore, c and k are linked only by a correlation of 0.45 for the curves of Fig. 1. A prior assumption that c = k may explain some of the predictive errors contained in other models of oxon levels. The caveat of the previous paragraph applies somewhat here also, however.

Finally, in Table 1 is presented the ratio A/b. This ratio is of importance to workers entering a field treated with the parent compound. It gives what one might term the oxon-exposure-potential for workers and equals the area under each curve of Fig. 1 were the curve extended to ∞ on the time axis. Areas under

TABLE 1
Derived constants for curves of Figure 1

Curve	A ($\mu g/cm^2$)	b (day^{-1})	c (day^{-1})	N_o ($\mu g/cm^2$)	k (day^{-1})	A/b ($\mu g\ day/cm^2$)
1	4.86	0.0035	0.300	21.8	0.11	1400
2	0.155	<0.0003	0.238	3.88	0.07	>500
3	0.215	0.063	0.970	3.25	0.22	3.4
4	0.102	0.096	2.00	0.793	0.14	1.1

A, b and c are the oxon curve constants. N_o and k are parent concentration at day 0 and dissipation rate constant, respectively.

the parent curve have been utilized often (cf., e.g., SERAT (1973)) in connection with the worker reentry problem because such areas incorporate information both on chemical level on the plant surface and duration of time the level exists. In the event a worker entered the field on day 0 and remained until oxon levels were imperceptible, he could be expected to acquire through contact with plant surfaces an amount of oxon proportional to A/b, a ratio seen in Table 1 to be of considerable variability. If the worker chooses to enter the field at a time T following parent application, the oxon-exposure-potential would be reduced by the factor exp (-bT), provided $c >> b$ as is usually the case.

It is important to recognize the utility of this model. In overall practice, the ratio of $N^{max} = A(b/c)^{b/(b-c)}$ to N_o is about 15%. The factors influencing constant b appear to be rainfall and dew (GUNTHER et al. 1977, NIGG 1980, SPENCER et al. 1975). Some progress has been made in identifying factors impinging on oxon growth, constant c (SPEAR et al. 1978). It appears to us that investigation of factors affecting oxon growth and dissipation would lead to regional estimation of potential worker reentry hazard from organophosphate pesticides.

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Accepted July 18, 1981